REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
28-12-2016	Final Report	1-Oct-2011 - 30-Sep-2015

4. TITLE AND SUBTITLE
Final Report: Synthesis and Characterization of Polymer-Metal Nanostructured Membranes

5a. CONTRACT NUMBER
W911NF-11-1-0486

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

6. AUTHORS
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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
59440-CH-H.9

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
Sulfonated poly(styrene-isobutylene-styrene) (SIBS) and sulfonated poly(ether-ether-ketone) (SPEEK) were studied after incorporating metallic counter-ions creating unique polymer-metal nanostructured membranes. A comprehensive materials characterization study was performed to understand their resulting nanostructure and their effect in the transport properties for direct methanol fuel cell (DMFC) applications and chemical and biological protective clothing (CBPC) applications. The unique interconnections created by the metallic counter-ions in the

15. SUBJECT TERMS
Block Copolymers, Morphology, Ionomers, Polymer Nanocomposite Membranes

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			David Suleiman
UU	UU	UU	UU		19b. TELEPHONE NUMBER 787-831-2065

Report Title

Final Report: Synthesis and Characterization of Polymer-Metal Nanostructured Membranes

ABSTRACT

Sulfonated poly(styrene-isobutylene-styrene) (SIBS) and sulfonated poly(ether-ether-ketone) (SPEEK) were studied after incorporating metallic counter-ions creating unique polymer-metal nanostructured membranes. A comprehensive materials characterization study was performed to understand their resulting nanostructure and their effect in the transport properties for direct methanol fuel cell (DMFC) applications and chemical and biological protective clothing (CBPC) applications. The unique interconnections created by the metallic counter-ions in the ionic domains produced enhanced selectivities for the transport of protons over methanol for DMFC applications and the transport of water over DMMP for CBPC applications.

Sulfonated fluoropolymers were also investigated. First the polymer-metal nanostructure of Nafion® with several counter-ions was studied upon supercritical fluid CO2 processing. Then, novel fluorinated block copolymers were synthesized using atom transfer radical polymerization (ATRP) and their resulting nanostructure was analyzed. The polymers synthesized included the following blocks: sulfonated polystyrene (SPS), poly(2,3,4,5,6-pentafluorostyrene) (P5FS), poly(4-fluorostyrene) (P4FS), and poly(2,2,3,4,4,4-hexafluorobutylmethacrylate) (HEMA). The effect of using different esterified initiators resulted in changes in the thermal properties, electronic configuration and eventually in improved transport properties for DMFC applications. The effect of varying the chemical blocks and their compositions also changed the resulting nanostructure, producing shorter interconnected ionic domains and higher water content, which resulted in the most improved transport properties for DMFC applications. Phase equilibria remain a critical issue for fluorinated polymers, as it can influence free-volume and water content, two important parameters that influence transport properties for the applications pursued.

Two Hispanic PhD students and twenty-five Hispanic undergraduate students worked in this investigation (70% females). Twelve of the Hispanic undergraduates that worked in this investigation continued graduate studies in Engineering (mostly PhDs). Four technical manuscripts were published from the results of this investigation, while one additional manuscript has been accepted for publication. Finally, the PI and his students delivered eighteen technical presentations in local, national and international meetings from the results of this investigation.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
12/28/2016	1	David Suleiman, Agnes M. Padovani, Arnaldo A. Negr┐on, James M. Sloan, Eugene Napadensky, Dawn M. Crawford. Mechanical and Chemical Properties of Poly(styrene-isobutylene-styrene): Effect of Sulfonation and Counter-Ion Substitution, Journal of Applied Polymer Science, (08 2013): 40344. doi:
12/28/2016	8	Edward M.A. Guerrero-Gutiérrez, Maritza Pérez-Pérez, Gregory M. Newbloom, Lilo D. Pozzo, David Suleiman. Morphology and Transport Properties of Sulfonated Fluoroblock Copolymer Blend Membranes, Polymer Engineering and Science, (12 2014): 0. doi:
12/28/2016	7	Maritza Perez-Perez, David Suleiman. Transport Properties of Sulfonated Poly(ether ether ketone) Membranes with Counter-Ion Substitution, Journal of Membrane Science, (12 2014): 414. doi:
12/28/2016	6	Edward M. A. Guerrero-Guti┐errez, Maritza P┐erez-P┐erez, David Suleiman. Synthesis and Characterization of Fluorinated Block Copolymer Membranes with Different Esterified Initiators for DMFC Applications, J Applied Polymer Science, (11 2014): 42046. doi:
TOTAL:		**4**

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper
TOTAL:	

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1. D. Suleiman. “Polymer Nanocomposite Membranes for Energy, Environmental and Biomedical Applications.” Colegio de Ingenieros y Agrimensores de Puerto Rico (CIAPR), Expo Cumbre 2016, San Juan, PR, May, 2016.

2. D. Suleiman. “Nanostructured Polymers: From Contemporary to Emerging Applications, CREST 2016 NanoDays Keynote, University of Puerto Rico, Mayaguez, PR, April,2016.

3. A. Millet, and D. Suleiman. “The Role of Water in Multi-Ionic Polymer Membranes)".ACS Jr. Technical Meeting, Ponce, PR, 2016.

4. M. Pérez and D. Suleiman. “Transport Properties of Sulfonated Poly(ether ether ketone) Membranes with Counter-Ion Substitution.” Oral Presentation at the 2015AIChENational Meeting, Salt Lake City, UT, November, 2015.

5. A. Millet and D. Suleiman “Sulfonation and Characterization of Poly(1,4-phenylene ether-ether-sulfone) (PEES) and Polyphenylsulfone (PPSF) for Fuel Cells and Specialty Separation Applications.” Poster Presentation at the 2015 ACS PRISM Meeting San Juan, PR March, 2015.

6. D. Suleiman“Polymer Nanocomposites: Technology for the XXI Century.”Oral Key Note Presentation at the 2014 Science & Materials Assembly. Mayaguez, PR, November, 2014.

7. M. Pérez and D. Suleiman Transport Properties of Sulfonated Poly(ether ether ketone) Membranes with Counter-Ion Substitution”. Poster Presentation at the 2014 AIChE National Meeting, Atlanta, GA, November, 2014.

8. M. Pérez and D. Suleiman. “Synthesis and Characterization of Poly(styrene-isobutylene-methyl vinyl ether) for Direct Methanol Fuel Cell Applications”. Poster Presentation at the 2014 AIChE National Meeting, Atlanta, GA, November, 2014.

9. D. Suleiman. “Functionalized Nanostructured Block Copolymer Ionomers for Fuel Cells and Specialty Separations” Oral Presentation during the 2014 Chemical Engineering Department Symposium (Key Note Speaker), University of Puerto Rico, Mayaguez, PR, May, 2014.

10. M. Pérez and D. Suleiman. “Transport Properties of Sulfonated Poly(ether ether ketone) Membranes with Counter-Ion Substitution”. Poster Presentation at the 2014 AIChE Southern Regional Meeting, San Juan, PR, March, 2014.

11. A. Millet, M. Pérez and D. Suleiman. “Effect of the Ether Block Position on Novel Copolymers for Fuel Cells and Specialty Separation Applications” Poster Presentation at the 2014AIChESouthern Regional Meeting, San Juan, PR, March, 2014.

12. A. Millet, M. Pérez and D. Suleiman. “Novel Block Copolymers as Proton Exchange Membranes for Fuel Cells and Specialty Separation Applications”.Poster Presentation at the 2013 AIChE National Meeting, San Francisco, CA, November, 2013.

13. E.M.A. Guerrero and D. Suleiman. “Nanostructure of a Novel Fluoroblock Copolymer using Atom Transfer Polymerization: Poly (styrene)-b-poly(2,3,4,5,6-Pentafluorostyrene)-b-poly(2,2,3,4,4,4-Hexafluorobutyl methacrylate)” Oral Presentation at the 2013 AIChE National Meeting, San Francisco, CA, November, 2013.

14. E.M.A. Guerrero and D. Suleiman. “Influence of initiator’s chemical composition during Atom Transfer Radical Polymerization of poly(styrene)-b-poly(2,2,3,4,4,4-hexafluorobutyl-methacrylate)” Oral Presentation at the 2013 AIChE National Meeting, San Francisco, CA, November, 2013.

15. A. Padovani, A. Negrón and D. Suleiman. “Mechanical Properties of Poly(styrene-isobutylene-styrene) Membranes as a Function of Sulfonation Level and Counter-Ion Substitution” Oral Presentation at the 2013 AIChE National Meeting, San Francisco, CA, November, 2013.

16. D. Suleiman. “Functionalized Nanostructured Block Copolymer Ionomers for Fuel Cells and Specialty Separations” Oral Presentation during the 2013 Chemistry Department Seminar, University of Puerto Rico, Mayaguez, PR, February, 2013.

17. D. Suleiman. “Functionalized Nanostructured Block Copolymer Ionomers for Fuel Cells and Specialty Separations” Oral Presentation during the 2012 Chemical Engineering Departmental Seminar Series, Drexel University, Philadelphia, PA, November, 2012.

18. E.M. Guerrero and D. Suleiman. “Synthesis and Characterization of Poly(styrene-b-4-fluorostyrene-isobutylene) Using Atom Transfer and Cationic Polymerization” Oral Presentation at the 2012 AIChE National Meeting, Pittsburgh, PA, October, 2012.

19. E. Guerrero and D. Suleiman. “Supercritical Fluid CO2 Processing and Counter-Ion Substitution of Nafion Membranes.” Presented at the ACS Jr. Technical Meeting, San Juan, PR, March, 2012.

Number of Presentations: 19.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

2015 Local Community Achievement Award, Buenaventura, Mayaguez, Puerto Rico

2015 Leadership Award, College of Engineering, University of Puerto Rico

2013 Distinguished Professor of Chemical Engineering, University of Puerto Rico

2012 Teaching Excellence Award, Chemical Engineering Dept., University of Puerto Rico

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Edward Guerrero	1.00	
Maritza Pérez	0.50	
FTE Equivalent:	**1.50**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
David Suleiman	0.25	
FTE Equivalent:	**0.25**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Alexander Millet	0.10	Chemical Engineering
Arnaldo Negrón	0.10	Chemical Engineering
FTE Equivalent:	**0.20**	
Total Number:	**2**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 2.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 2.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 2.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 2.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME	
Total Number:	

Names of personnel receiving PHDs

NAME	
Edward Guerrero	
Total Number:	**1**

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attachment

Technology Transfer

Interaction with DOD personnel in ARL resulted in one technical publication and several technical discussions.

Synthesis and Characterization of Polymer-Metal Nanostructured Membranes
W911NF-11-1-0486, Final Technical Report
01 Oct 2011 – 31 Oct 2015, David Suleiman, PI (University of Puerto Rico at Mayaguez)

Abstract

Sulfonated poly(styrene-isobutylene-styrene) (SIBS) and sulfonated poly(ether-ether-ketone) (SPEEK) were studied after incorporating metallic counter-ions creating unique polymer-metal nanostructured membranes. A comprehensive materials characterization study was performed to understand their resulting nanostructure and their effect in the transport properties for direct methanol fuel cell (DMFC) applications and chemical and biological protective clothing (CBPC) applications. The unique interconnections created by the metallic counter-ions in the ionic domains produced enhanced selectivities for the transport of protons over methanol for DMFC applications and the transport of water over DMMP for CBPC applications.

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Two Hispanic PhD students and twenty-five Hispanic undergraduate students worked in this investigation (70% females). Twelve of the Hispanic undergraduates that worked in this investigation continued graduate studies in Engineering (mostly PhDs). Four technical manuscripts were published from the results of this investigation, while one additional manuscript has been accepted for publication. Finally, the PI and his students delivered eighteen technical presentations in local, national and international meetings from the results of this investigation.

1.0 Statement of the Problem Studied

There is a need for the US military forces to respond to diverse scenarios protected from chemical and biological attacks. Chemical and biological protective clothing (CBPC) is one tool the soldier could have to protect him/herself from toxic agents. In the past, one of the most common materials used for CBPC was butyl rubber (BR). Although BR blocks most harmful agents, it does not allow water (from sweat) to escape, thus causing heat fatigue and exhaustion.[1] One alternative to this problem has been using thermoplastic elastomers (TPE) with rubbery and glassy thermodynamically immiscible microphases. The glassy segment is often composed of polystyrene, which can be sulfonated to high ion exchange capacities (IEC)[2], creating ion containing polymers also called ionomers. The sulfonation often occurs in the para- position, and the highly sulfonated polymers form a complex tri-dimensional network with three distinct phases: the rubbery phase (*e.g.,* polyisobutylene), the glassy phase (*e.g.,* polystyrene), and the interconnected sulfonic groups that allow water vapor to permeate after a certain percolation threshold has been obtained.[3] These ionomers have become an attractive alternative to BR at high sulfonation levels and significant advances have been made studying sulfonated poly(styrene-ethylene-butylene-styrene) (SEBS), and sulfonated poly(styrene-isobutylene-styrene) (SIBS) with 30 wt% polystyrene and number average molecular weight (Mn) of 65,000.[4-6] Despite all the advances, the permeability of dimethylmethylphosphonate (DMMP), which is chemically similar to the nerve agent Sarin (GB), is of the same order of magnitude as water, thus creating a selectivity very close to one.[6] The limitations in selectivity have been both chemical as well as physical (*e.g.,* morphology) in these complex three-dimensional structures. One approach to pursue higher selectivities is cross-linking the sulfonic groups of the membranes with a cation. Previous investigations evaluating several +2 cation-exchanged SIBS (Mg^{+2}, Ca^{+2}, Ba^{+2}) improved the selectivity of the membranes by one order of magnitude, since the cation makes it more difficult for the toxin to be transported[7]. However, SAXS data has shown that the use of cations for the highly sulfonated SIBS maintains the lamellar structure, while the distance between layers remains unchanged. These results motivated the study of polymer-metal nanostructured membranes, but with different polymers, primarily fluoroelastomers.

Fluoropolymers such as Nafion® are the most commonly used proton exchange membranes (PEM) in direct methanol fuel cells (DMFC). Their fluoroelastomeric components act as barriers, while their ionic sulfonic domains allow for the transport of protons and other ionic species through the membrane. However, without additional modifications they posses poor selectivity, such as high methanol permeability (also known as the methanol cross-over problem) limiting the performance of DMFC. One approach for reducing the methanol permeability has been chemically modifying it with acidic inorganic/organic materials (*e.g.,* cations, inorganic fillers-like SiO_2, zeolites).[8-14] These fillers partially block the nanochannels, while their surface acidity maintain a high conductivity of the resulting membranes, since proton migration inside the membrane is assisted by the water molecules on the surface of the additive. Molecular dynamic simulations of perflurosulfonic acid (PFSA) membranes suggest that the most significant parameter for controlling the water clustering and therefore influence chemical, mechanical and transport properties is the length of the side chain to which the sulfonic acid group is attached.[15] Unfortunately, this and other important parameters such as surface acidity and pore structure have not been studied due to phase equilibria considerations.

In recent years, the introduction of atom transfer radical polymerization (ATRP) has revitalized the concept of controlled/living polymerization and allowed the introduction of useful functionalities and polymers with novel architectures and properties.[16-17]ATRP is a radical process much more tolerant of functional groups than ionic polymerization; therefore, allowing for the polymerization and co-polymerization of new block copolymers, including fluoroelastomers with glassy polymers (like polystyrene, PS) that can be sulfonated to high ion exchange capacity (IEC).

The first year of this investigation new fluoropolymers were synthesized using ATRP. Some of the initial materials characterizations were also performed. The second year of the investigation all the block copolymers had been synthesized and some of the materials characterization studies were completed. Phase equilibria limited the formation of the resulting polymer membranes, which led to the study of different solvents, blends and block composition. During the third year of this investigation, the materials characterization and transport studies were completed for the novel fluorinated block copolymers with respect to two major variables: initiator type and block composition. In addition, two sulfonated block polymers were studied after metallic counter-ion substitution. The resulting nanostructure shows unique changes in the transport properties of protons and methanol for DMFC applications, especially for the polymer with additional ionic domains. The coordination of the counter-ions (and their new interconnections), the role of water and the resulting free-volume play a critical role in the resulting transport mechanism for the applications pursued.

2.0 Summary of the Most Significant Results

Technical details are included in the peer-reviewed manuscripts that were published as a result of this investigation.

2.1 Sulfonated Block Copolymers

2.1.1 Mechanical and Chemical Properties of Sulfonated Poly(styrene-isobutylene-styrene): Effect of Sulfonation and Counter-Ion Substitution

See attached manuscript published in the Journal of Applied Polymer Science:

D. Suleiman, A.M. Padovani, J. M. Sloan, E. Napadensky and D. M. Crawford*.* *"Mechanical and Chemical Properties of Poly(styrene-isobutylene-styrene) Block Copolymers: Effects of Sulfonation and Counter Ion Substitution". Journal of Applied Polymer Science*, 131 (11), 5620-5628, **2014**.

2.1.2 Transport Properties of Sulfonated Poly(ether-ether-ketone) with Counter-Ion Substitution

See attached manuscript published in the Journal of Membrane Science:

M. Pérez-Pérez and D. Suleiman. *"Transport Properties of Sulfonated Poly(ether ether ketone) with Counter-Ion Substitution". Journal of Membrane Science, 493, 414-427,* **2015**.

2.2 Fluoropolymers

2.2.1 Supercritical Fluid CO_2 Processing and Counter-Ion Substitution of Nafion® Membranes

See attached manuscript published in the Journal of Applied Polymer Science:

E.M. Guerrero-Gutiérez and D. Suleiman.*"Supercritical Fluid CO_2 Processing and Counter-Ion Substitution of Nafion® Membranes". Journal of Applied Polymer Science*, 129 (1), 73-85, **2013**.

2.2.2 Synthesis and Characterization of Sulfonated Fluorinated Block Copolymer Membranes with Different Esterified Initiators for DMFC Applications

See attached manuscript published in the Journal of Applied Polymer Science:

E.M.A. Guerrero-Gutiérrez, M. Pérez-Pérez and D. Suleiman. *"Synthesis and Characterization of Sulfonated Fluorinated Block Copolymer Membranes with Different Esterified Initiators for DMFC Applications". Journal of Applied Polymer Science, 132, 42046,* **2015**.

2.2.2 Morphology and Transport Properties of Sulfonated Fluoroblock Copolymer Blend Membranes

See attached manuscript submitted to the Journal of Applied Polymer Science:

E.M.A. Guerrero-Gutiérrez, M. Pérez-Pérez and D. Suleiman. *"Morphology and Transport Properties of Sulfonated Fluoroblock Copolymer Blend Membranes". Accepted for Publication, Polymer Engineering and Science,* **2016**.

3.0 References

1. Lee, B., Yang, T., and Wilusz, E. *Polymer Engineering &*Science, 36, 9, 1217, **1996**.
2. Elabd, Y, E., Napadensky, E. *Polymer*, 45, 3037, **2004**.
3. Hsu, W.Y., Barkley, J.R., and Meakin, P. *Macromolecules*, 13, 198, **1980**.
4. Elabd, Y, E., Napadensky, E., Sloan, J.M., Crawford, D.M., and Walker, C.W. *J. of Membrane Science,* 217, 227, **2003**.
5. Elabd, Y, E., Walker, C.W. and Beyer, F.L. *J. of Membrane Science*, 231, 181, **2004**.
6. Napadensky, G., Sloan, J.M., and Crawford, D.M., ACS National Conference, San Francisco, CA (**2006**).
7. Suleiman, D., Carreras, G., Soto, Y*. In Press, Journal of Applied Polymer Science*, **2012***.*
8. Arico, A.S., Baglio, V., Blasi, A.D., Antonucci, V. *Electrochem. Comm..,* 5, 862, **2003**.
9. Lee, K, et al., *Electrochem. Commun.*, 7, 113, **2005**
10. Baglio, V., Arico, A.S., Blasi, A.D., Creti, P., Antonucci, V., Antonucci, P.L. *Electrochem Acta,* 50, 1241, **2005**.
11. Bauer, F., Willert-Porrada, M. *J. of Membrane Science*, 233, 141, **2004**.
12. Lin, C.W., Fan, K.C., Thangamuthu, R. *J. of Membrane Science*, 278, 437, **2006**.
13. Daiko, Y., Klein, L.C., Kasuga, T., Nogami, M. *J. of Membrane Science*, 281, 619, **2006**.

14. Nagarale, R,K, Shin, W., Singh, P.K. *Polymer*, 1, 388, **2010**.
15. Liu, J., Suraweera, N., Keffer, D.J., Cul, S, Paddison, S.J. *J. Phys. Chem.*, 114, 11279, **2010**.
16. Matyjaszewski, K. *ACS Symposium Series*, 768, Chapter 1, 2, **2000**.
17. Tsarevski, N., Sarbo,u, T., Belt, B., Matyjaszewski, K. *Macromolecules*, 35, 6142, **2002**.
18. Suleiman, D., Elabd, Y.A., Napadensky, E., Sloan, J.M., and Crawford, D.M. *Thermochimica Acta*, 430, 149, **2005**.
19. Suleiman, D., Napadensky, E., Sloan, J.M., and Crawford, D.M. *Thermochimica Acta*, 460, 35-40, **2007**.
20. Suleiman, D. Carreras, G., Soto Y. *Journal of Applied Polymer Science*, 128 (4), 2297-2306, **2013**.
21. Avilés S.L., Suleiman, D. *Journal of Applied Polymer Science*, 129 (4), 2294-2304, **2013**.
22. Avilés, S.M., Suleiman, D. *J. of Membrane Science*, 362, 471-477, **2010**.
23. Yeo S.D., Kiran E. *J. of Supercritical Fluids,* 34, 287, **2005**.
24. Gribov, E.N. et al J*. of Membrane Science*, 297, 1, **2007**.